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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

A series of ((trimethylsilyl)methyl)gallium (I) compounds, $M_I Ga(CH_2SiMe_3)_2$ (M_I = Na, K) and $M_I Ga(CH_2SiMe_3)_2 \cdot MeOC_2H_4OMe$ (M_I = Li, Na) have been prepared and fully characterized by elemental analyses, cryoscopic molecular weight measurements in benzene solution, solubility properties and infrared, ^1H and ^{13}C NMR spectral data. These novel compounds represent

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a new class of organometallic derivative, which incorporate low oxidation state, main-group, metallic anions. The preparative route to these organo-gallium(I) compounds involves an apparent reductive elimination reaction between $Ga(CH_2SiMe_3)_3$ with alkali-metal hydrides in benzene or dimethyoxy-ethane. All available data including the high solubility in aliphatic and aromatic solvents, low melting points and molecular weight measurements are consistent with the following covalent molecular formulas: $[KGa(CH_2SiMe_3)_2]_2$, $[NaGa(CH_2SiMe_3)_2]_3$ and $[LiGa(CH_2SiMe_3)_2 \cdot MeOC_2H_4OMe]_x$. Structures involving gallium-gallium bonds are proposed to account for observed molecular associ-ation and chemical properties.

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Organometallic Gallium(I) Anions

Prepared by a Reductive Elimination Reaction
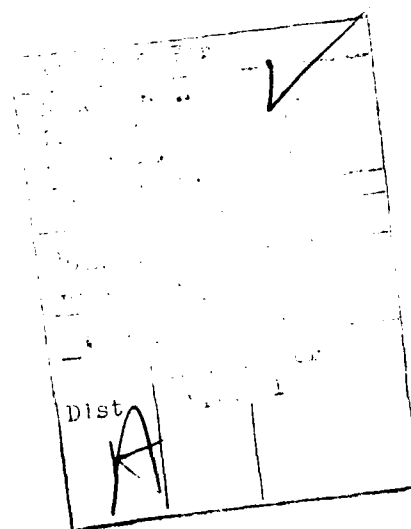

by

O. T. Beachley, Jr. and R. G. Simmons

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Organometallic Gallium(I) Anions

Prepared by a Reductive Elimination Reaction

by

O. T. Beachley, Jr.[*] and Randall G. Simmons

Abstract

A series of ((trimethylsilyl)methyl)gallium (I) compounds,
$M_I Ga(CH_2 SiMe_3)_2$ (M_I = Na, K) and $M_I Ga(CH_2 SiMe_3)_2 \cdot MeOC_2 H_4 OMe$ (M_I = Li,
Na) have been prepared and fully characterized by elemental analyses,
cryoscopic molecular weight measurements in benzene solution, solubility
properties and infrared, ^{1}H and ^{13}C NMR spectral data. These novel
compounds represent a new class of organometallic derivative, which
incorporate low oxidation state, main-group, metallic anions. The pre-
parative route to these organogallium(I) compounds involves an apparent
reductive elimination reaction between $Ga(CH_2 SiMe_3)_3$ with alkali-metal
hydrides in benzene or dimethoxyethane. All available data including
the high solubility in aliphatic and aromatic solvents, low melting
points and molecular weight measurements are consistent with the fol-
lowing covalent molecular formulas: $[KGa(CH_2 SiMe_3)_2]_2$, $[NaGa(CH_2 SiMe_3)_2]_3$
and $[LiGa(CH_2 SiMe_3)_2 \cdot MeOC_2 H_4 OMe]_x$. Structures involving gallium-gallium
bonds are proposed to account for observed molecular association and
chemical properties.

Introduction

Organometallic compounds have been known for over 100 years. Much of the development of the chemistry of the transition-metal derivatives can be ascribed to the synthetic utility of redox reactions and metal carbonyl anions.[1] In contrast the chemistry of the organometallic derivatives of the main-group elements has focused on the properties and reactions of compounds with the metals in their highest oxidation states.[2] Consequently, the literature contains very few examples of well-defined, kinetically stable, low oxidation state organometallic compounds or of reactions in which the main-group metal in an organometallic derivative changes oxidation state. The compounds,[3,4] $In(C_5H_5)$ and $Tl(C_5H_5)$, are the only examples of low oxidation state Group III organometallic derivatives. Both of these compounds[5,6] exist in the solid state as linear polymers with the cyclopentadienyl ring exhibiting pentahapto coordination. In Group IV chemistry, the unique low oxidation state compounds[7] $M_{IV}(CH(SiMe_3)_2)_2$ (M_{IV} = Ge, Sn, Pb) have been prepared and thoroughly characterized. An X-ray structural study[8] of the tin compound confirms a dimeric structure which has an apparent bent tin-tin double bond using the available electron pair and vacant orbital on each tin(II) atom.

The two potential routes to low oxidation state main-group organometallic compounds involve the alkylation of a low oxidation state halogen compound or the reduction of a high oxidation state organometallic derivative. The alkylation reaction has been applied to the syntheses of the $M_{IV}(CH(SiMe_3)_2)_2$ compounds from $M_{IV}Cl_2$ and the lithium

alkyl.[7] In contrast the synthesis[3,8] of $In(C_5H_5)$ involves a reduction reaction since the starting material is $InCl_3$. The cyclopentadienide anion[8] is considered the reducing agent for $In(C_5H_5)_3$. Regrettably, both of these observed reactions are of limited use for the synthesis of other Group III derivatives. The common low oxidation state halogen compounds incorporate the metal in both the low and high oxidation states,[9] for example $Ga^+GaCl_4^-$.

The chemistry of the hydride derivatives of the heavier main-group metals suggest the potential occurrence of facile reduction reactions at the metallic center. Previous research[10] has shown $(HGaCl_2)_2$ to quantitatively form $Ga^+GaCl_4^-$ and H_2 at 25°. Trichlorogermane,[11] $HGeCl_3$, undergoes rapid evolution of HCl at 50° to generate the low oxidation state compound, $GeCl_2$. This latter reaction is an apparent example of reductive elimination, a class of reaction which has been of little synthetic utility in main-group chemistry. Thus, a controlled reduction reaction of a hydride derivative might be a possible route to a kinetically stable, low oxidation state organometallic compound if associative and dissociative low energy decomposition pathways for the product can be avoided. The ligands, CH_2SiMe_3, $CH(SiMe_3)_2$ and $N(SiMe_3)_2$, have been observed to minimize the availability of these types of decomposition pathways.[12] Thus, the reactions of tris((trimethylsilyl)methyl)gallium (III) with alkali-metal hydrides were investigated as possible routes to low oxidation state gallium compounds. In this paper we report the syntheses and characterizations of organogallium compounds with the simplest formula, $KGa(CH_2SiMe_3)_2$ and $NaGa(CH_2SiMe_3)_2$. Since these for-

mulas are consistent with the gallium being in the +1 oxidation state,
these compounds represent a new clas' of organometallic derivative,
which incorporate low oxidation state, main-group metallic anions. The
nature of the synthetic reaction path, the unusual properties of these
novel compounds and their possible structures based on available data
are discussed.

Experimental

<u>Materials.</u> All compounds described in this investigation were extremely
oxygen and moisture sensitive and were manipulated in a vacuum line or a
purified nitrogen or argon atmopshere. The solvents were purified by
refluxing with an appropriate drying agent and vacuum distilled just
prior to use. The drying agents for the solvents dimethoxyethane,
benzene and methylene chloride were sodium-benzophenone ketyl, sodium
ribbon and phosphorus pentoxide, respectively. The alkali-metal hydrides
were purchased from Alfa Inorganics as an oil dispersion. The oil was
removed by repeated extraction with dry pentane. Tris((trimethylsilyl)-
methyl)gallium (III),[13] $Ga(CH_2SiMe_3)_3$, was prepared from $GaCl_3$ by a
standard Grignard reaction in diethylether.

<u>Synthesis of ((Trimethylsilyl)methyl)gallium (I) Compounds:</u>

<u>$M_IGa(CH_2SiMe_3)_2$ (M_I = Na, K) and $M_IGa(CH_2SiMe_3)_2 \cdot MeOC_2H_4OMe$ (M_I = Li, Na).</u>
The low oxidation state derivatives $M_IGa(CH_2SiMe_3)_2$ (M_I = Na, K) and
$M_IGa(CH_2SiMe_3)_2 \cdot MeOC_2H_4OMe$ (M_I = Li, Na) were prepared from $Ga(CH_2SiMe_3)_3$
and the appropriate alkali-metal hydride in benzene or dimethoxyethane,
respectively. The nature of the product depends on both the reducing

agent and solvent. To illustrate the experimental procedure, the preparation of $NaGa(CH_2SiMe_3)_2$ is described in detail. All other compounds were prepared in a similar manner. Table I gives the specific reaction conditions, melting point data and the percent yields of products. Analytical data for the new compounds are given in Table II, molecular weight, infrared and NMR data in appropriate sections.

A 250 mL heavy wall pyrolysis tube equipped with a side arm break-seal was charged with 1.726 g (5.213 mmol) $Ga(CH_2SiMe_3)_3$ and 0.313 g (13.0 mmol) NaH in the dry box. Then, all of the following manipulations were carried out with the apparatus under high vacuum. Dry benzene, 20 mL, was distilled into the tube using a -196° bath. The tube was sealed and the reaction mixture heated at 45° with stirring for 24 hr. After the break-seal was opened, the reaction mixture was filtered to remove unreacted NaH. The volatile components were then separated by fractional distillation to yield benzene (-78° trap) and 0.452 g (5.13 mmol, 98.5% yield) tetramethylsilane (-196° trap). The product, $NaGa(CH_2SiMe_3)_2$, was isolated as a colorless, crystalline solid (1.362 g, 5.098 mmol, 97.8% yield). No further purification was necessary.

The new low oxidation state compounds, $NaGa(CH_2SiMe_3)_2$, $KGa(CH_2SiMe_3)_2$ and $NaGa(CH_2SiMe_3)_2 \cdot MeOC_2H_4OMe$, are very soluble in aliphatic and aromatic solvents as well as the more polar solvents methylene chloride, acetonitrile and diethylether. In contrast, the lithium derivative, $LiGa(CH_2SiMe_3)_2 \cdot MeOC_2H_4OMe$, has only limited solubility in n-pentane and benzene but is readily soluble in the polar solvents, dimethoxyethane and tetrahydrofuran.

<u>Analyses</u>   The new ((trimethylsilyl)methyl)gallium (I) compounds were analyzed for gallium by EDTA titration.[14]   The percentages of alkali metals (Li, Na, K) were determined by standard atomic absorption procedures using a Perkin-Elmer Model 503 spectrometer.   The mmol of CH_2SiMe_3 groups per mol gallium was determined by quantitatively converting the ligand into $Si(CH_3)_4$ by reaction of the organogallium(I) compound with anhydrous hydrogen chloride in benzene solution at room temperature.   The $Si(CH_3)_4$ was separated from all other volatile components in the reaction mixture by passage through a -78° trap and into a -196° trap on the vacuum line.   The purity of the $Si(CH_3)_4$ was confirmed by vapor pressure measurements and ^{1}H NMR and infrared spectroscopy.   All analytical data are given in Table II.

<u>Molecular Weight Studies</u>   Molecular weight measurements were obtained cryoscopically in benzene by using an instrument similar to that described by Shriver.[15]   The following molecular weight data for the new ((trimethylsilyl)methyl)gallium (I) compounds were observed. $NaGa(CH_2SiMe_3)_2$ (formula wt 267):   Calc. molality monomer, (observed molecular weight). 0.2655(811), 0.1610(809), 0.1334(816), 0.0834(807); $KGa(CH_2SiMe_3)_2$ (formula wt 284):   0.2165(572), 0.1460(572), 0.1355(568), 0.1138(572); $NaGa(CH_2SiMe_3)_2 \cdot MeOC_2H_4OMe$ (formula wt 357):   0.0930(854), 0.0917(827), 0.0761(778), 0.0505(722), 0.0462(699), 0.0320(604); $LiGa(CH_2SiMe_3)_2 \cdot MeOC_2H_4OMe$ (formula wt 341):   Compound has insufficient solubility in benzene for molecular weight measurements.

<u>Infrared Spectra</u>   The infrared spectra were recorded in the range 4000-250 cm^{-1} by means of a Perkin-Elmer Model 457 spectrometer.   The spectra were recorded as Nujol mulls using CsI plates.   Absorption

Table I

Reactions of $Ga(CH_2SiMe_3)_3$ with Alkali-metal Hydrides

Compound	Reaction Conditions Solvent/Time(hrs)/Temperature (°C)	Percent Yield of Products[a] Si(CH₃)₄	Ga(I) Compound	Melting Point °C
$NaGa(CH_2SiMe_3)_2$	$C_6H_6/24/45°$	98.5	97.8	59-60°
$KGa(CH_2SiMe_3)_2$	$C_6H_6/24/45°$	98.8	97.3	74-75°
$NaGa(CH_2SiMe_3)_2 \cdot MeOC_2H_4OMe$	$MeOC_2H_4OMe/24/25°$	99.0	98.8	100-102°
$LiGa(CH_2SiMe_3)_2 \cdot MeOC_2H_4OMe$	$MeOC_2H_4OMe/168/45°$	97.1	94.8	80-82°

[a]The percent yields of products, $Si(CH_3)_4$ and organogallium(I) compounds, are based upon initial amounts of $Ga(CH_2SiMe_3)_3$ used in the preparative reaction.

-8-

Table II

Analytical Data for the Alkali-Metal ((Trimethylsilyl)methyl)gallium (I) Compounds

| Compound | Gallium Analysis | | Alkali Metal Analysis | | Mole Ratio |
	% Calc.	% Found	% Calc.	% Found	(CH_2SiMe_3/Ga)
$NaGa(CH_2SiMe_3)_2$	26.10	26.09	8.61	8.64	2.00
$KGa(CH_2SiMe_3)_2$	24.62	24.51	13.80	13.73	2.00
$NaGa(CH_2SiMe_3)_2 \cdot MeOC_2H_4OMe$	19.51	19.52	6.44	6.41	1.98
$LiGa(CH_2SiMe_3)_2 \cdot MeOC_2H_4OMe$	20.43	20.38	2.03	2.04	a

[a]Due to the limited solubility of $LiGa(CH_2SiMe_3)_2 \cdot MeOC_2H_4OMe$ in solvents useful for the quantitative formation and isolation of $Si(CH_3)_4$, the analytical data could not be obtained.

intensities were measured by using the method of Durkin, Glore and DeHayes.[16]

Following are the spectral data: frequency, cm^{-1} (intensity: vs, very strong, s, strong; m, medium; w, weak; sh, shoulder). Bands due to mulling agents have been omitted. $NaGa(CH_2SiMe_3)_2$: 1265 (s), 1252 (s), 1252 (vs), 981 (s), 960 (s), 855 (vs), 835 (vs), 765 (m), 735 (m), 691 (w), 565 (w), 509 (s), 480 (m).

$KGa(CH_2SiMe_3)_2$: 1251 (s), 1238 (vs), 970 (s), 947 (s), 856 (vs), 834 (vs), 763 (m), 743 (m), 680 (w), 564 (w), 504 (s), 483 (m).

$LiGa(CH_2SiMe_3)_2 \cdot MeOC_2H_4OMe$: 1255 (s), 1244 (vs), 1200 (m), 1130 (m), 1084 (m), 1032 (w), 969 (s), 865 (vs), 840 (vs), 770 (s), 765 (s), 699 (m), 559 (m), 518 (s), 481 (w).

$NaGa(CH_2SiMe_3)_2 \cdot MeOC_2H_4OMe$: 1255 (s), 1245 (vs), 1198 (m), 1122 (m), 1085 (m), 982 (s), 960 (s), 855 (vs), 825 (vs), 760 (s), 740 (s), 685 (m), 565 (w), 508 (s), 475 (m).

Nuclear Magnetic Resonance Spectra: The ^1H NMR spectra were recorded at 100 MHz and ambient temperature by using a Joelco Model MH-100 spectrometer. All chemical shifts (τ) are given in ppm (Table III) and are referenced to tetramethylsilane as 10.00 ppm. The ^1H NMR spectra for all ((trimethylsilyl)methyl)gallium (I) compounds were observed as methylene chloride solutions.

The ^{13}C NMR spectra of d^6-benzene solutions were recorded at 25.2 MHz and ambient temperature using a Varian XL-100 spectrometer. All chemical shifts (ppm) are referenced to tetramethylsilane and are downfield of it. $[KGa(CH_2SiMe_3)_2]_2$ 4.49 ($SiCH_2$), 3.91 (SiMe); [NaGa-

$(CH_2SiMe_3)_2]_3$ 4.05 ($SiCH_2$), 3.85 (SiMe); $Ga(CH_2SiMe_3)_3$ 13.29 ($SiCH_2$), 3.06 ($SiCH_3$).

Lewis Acidity Studies:

The Lewis acidities of the ((trimethylsilyl)methyl)gallium (I) compounds, $M_IGa(CH_2SiMe_3)_2$ (M_I = Na, K), were studied by reacting a stoichiometric quantity of the desired acid with excess base (trimethylamine, acetonitrile, diethylether, tetrahydrofuran and dimethoxyethane). The reaction mixture was stirred at room tempearature for two hours. The volatile components were then removed until no dissociation pressure was observed. If a stoichiometric quantity of base was retained by the acid, the stable adduct was characterized by its ^{1}H NMR spectrum (Table III). In those cases in which a non-stoichiometric quantity of base was retained, the product was not further characterized.

Stable 1:1 adducts were isolated at room temperature for the following acid-base pairs: $KGa(CH_2SiMe_3)_2$ - dimethoxyethane, $NaGa(CH_2SiMe_3)_2$ - dimethoxyethane, - tetrahydrofuran and - trimethylamine.

Results and Discussion

A novel class of organometallic derivatives of gallium as exemplified by $KGa(CH_2SiMe_3)_2$, $NaGa(CH_2SiMe_3)_2$ and $LiGa(CH_2SiMe_3)_2 \cdot MeOC_2H_4OMe$ have been prepared by a new synthetic reaction and fully characterized. The composition of these sharp-melting, colorless, crystalline solids are consistent with gallium being classified in the +1 oxidation state. Thus, these novel, kinetically stable, low oxidation state compounds represent the first examples of anionic, sigma-bonded organometallic derivatives of gallium (I).

The new gallium (I) compounds were prepared from tris((trimethyl-

Table III

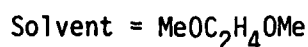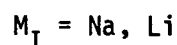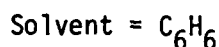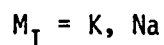Proton NMR Data for the Alkali-metal ((Trimethylsilyl)methyl)gallium
(I) Compounds and their Lewis Acid Base Adducts[a]

Compound	Si-CH$_3$ protons (ppm)	Si-CH$_2$ protons (ppm)	Lewis Base Protons[b] (ppm)		
LiGa(CH$_2$SiMe$_3$)$_2$MeOC$_2$H$_4$OMe	9.96	10.18	singlet	CH$_2$	6.41
			singlet	CH$_3$	6.57
NaGa(CH$_2$SiMe$_3$)$_2$	9.95	10.80	————		
NaGa(CH$_2$SiMe$_3$)$_2$MeOC$_2$H$_4$OMe	9.93	10.55	singlet	CH$_2$	6.39
			singlet	CH$_3$	6.55
NaGa(CH$_2$SiMe$_3$)$_2$O(CH$_2$)$_4$	9.92	10.63	multiplet	CH$_2$	6.15
			multiplet	CH$_2$	8.05
NaGa(CH$_2$SiMe$_3$)$_2$ N(CH$_3$)$_3$	9.95	10.67	singlet	CH$_3$	7.79
KGa(CH$_2$SiMe$_3$)$_2$	9.93	10.01	————		
KGa(CH$_2$SiMe$_3$)$_2$MeOC$_2$H$_4$OMe	9.92	10.14	singlet	CH$_2$	6.64
			singlet	CH$_2$	6.61

[a] Chemical shifts (τ) are given in ppm relative to tetramethylsilane.
Methylene chloride was used as solvent.

[b] The chemical shifts (ppm) for the non-adducted Lewis Base-protons in
methylene chloride relative to Si(CH$_3$)$_4$ are the following: dimethoxy-
ethane, singlet CH$_2$ (6.57), singlet CH$_3$ (6.72); tetrahydrofuran,
multiplet α-CH$_2$ (6.40), multiplet β-CH$_2$ (8.25), trimethylamine, singlet
CH$_3$ (7.79).
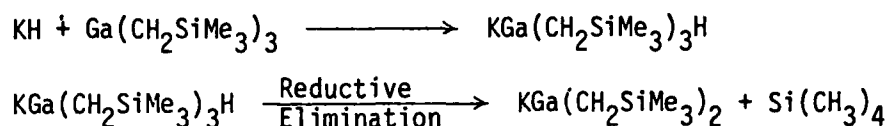
sily)methyl)gallium (III), $Ga(CH_2SiMe_3)_3$, and an alkali-metal hydride by a stoichiometric reaction as summarized by the following idealized equation. There are several aspects of this particular reaction which

$$Ga(CH_2SiMe_3)_3 + M_IH \xrightarrow{\text{Solvent}} M_IGa(CH_2SiMe_3)_2 + Si(CH_3)_4$$

M_I = K, Na   Solvent = C_6H_6

M_I = Na, Li   Solvent = $MeOC_2H_4OMe$
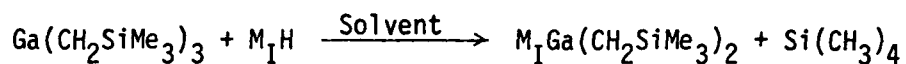
are synthetically and experimentally attractive. The specific nature of the gallium (I) product can be easily changed by using different alkali-metal hydrides and solvents in a reaction which is carried out under very mild conditions. When benzene is used as solvent only KH and NaH react at 45° to form the simple compounds, $KGa(CH_2SiMe_3)_2$ and $NaGa(CH_2SiMe_3)_2$. In the case of dimethoxyethane, lower reaction temperatures (25°) can be employed, but the final product incorporates a mole of solvent, $NaGa(CH_2SiMe_3)_2 \cdot MeOC_2H_4OMe$ and $LiGa(CH_2SiMe_3)_2 \cdot MeOC_2H_4OMe$. Since the gallium (I) product is soluble in the reaction medium, the excess, insoluble metal hydride is easily separated by simple filtration. Finally, the extent of reaction is readily monitored by the evolution of tetramethyl-silane. The reaction is observed to be stoichiometric, giving essentially quantitative yields of both tetramethylsilane and the gallium (I) product (Table I).

The stoichiometry of the preparative reaction, the analytical data and the chemical and spectral properties of the products confirm the occurrence of an oxidation-reduction reaction. The gallium (III) reac-tant is converted to a gallium (I) product, a reduction process. The only other product, $Si(CH_3)_4$, must then be the product of the oxidation reaction. The following reaction sequence summarizes the proposed path

for KH but it is equally applicable to the other metal hydrides. All

experimental data suggest that the gallium (I) product is formed by a

$$KH + Ga(CH_2SiMe_3)_3 \longrightarrow KGa(CH_2SiMe_3)_3H$$

$$KGa(CH_2SiMe_3)_3H \xrightarrow{\text{Reductive}}_{\text{Elimination}} KGa(CH_2SiMe_3)_2 + Si(CH_3)_4$$

reductive elimination reaction of a gallium (III) hydride intermediate,

$KGa(CH_2SiMe_3)_3H$. The gallium (III) hydride intermediate is formed in a

Lewis acid-base reaction between $Ga(CH_2SiMe_3)_3$ and the alkali-metal

hydride, a thoroughly studied class of reactions for electron-deficient

compounds.[2] The observed order of reactivity of the different metal

hydrides for forming the gallium (I) products, KH > NaH > LiH, is iden-

tical to that observed for forming the simple Lewis acid-base adducts of

the aluminum alkyls,[2] $MAlR_3H$. Thus, a primary factor controlling reac-

tivity is probably related to the relative magnitude of the lattice

energies of the alkali-metal hydrides. The quantitative formation of

products in the preparative reaction, the lack of any infrared bands in

the 2100-1800 cm^{-1} region and the analytical data confirm that the

gallium (III) hydride intermediate is readily converted to the gallium

(I) product. The nature of the proposed facile reductive elimination

reaction (Step 2) was investigated using NaD. Mass spectral data show

that the deuterium is quantitatively incorporated into the tetramethyl-

silane as $(CH_3)_3SiCH_2D$. These results suggest that the reductive elim-

ination reaction might occur as a non-radical, possibly concerted,

process. Non-radical reactions should produce only $(CH_3)_3SiCH_2D$, where-

as the existence of radical paths would lead to $Si(CH_3)_4$ by hydrogen

abstraction from the solvent.

The new organometallic gallium (I) compounds have properties of typical covalent substances - low melting points and solubility in hydrocarbon solvents. The cryoscopic molecular weight measurements in benzene solution indicate that molecular association is an important structural feature for these compounds. The potassium derivative, $[KGa(CH_2SiMe_3)_2]_2$ exists in benzene solution as a dimer whereas $[NaGa(CH_2SiMe_3)_2]_3$ is a trimer. These degrees of molecular association suggest that the properties of the alkali-metal ions, including their steric and thermo-dynamic effects, influence the specific nature of the molecule. The unique solubility properties and low melting points of the gallium (I) compounds are also consistent with relatively weak interactions between associated molecular units. The structures and nature of bonding of the molecules, infrared, ^1H and ^{13}C NMR data, and Lewis acidity studies for these gallium (I) compounds will be discussed in turn.

Molecular association of the monomeric formula units can occur by metal-metal or alkyl bridge bonding. All available data suggest that both the dimer, $[KGa(CH_2SiMe_3)_2]_2$, and trimer, $[NaGa(CH_2SiMe_3)_2]_3$, exist with metal-metal bonds. The proposed dimeric structure for $[KGa(CH_2SiMe_3)_2]_2$ (Figure 1) is analogous to that defined by an X-ray structural study[7] for $[Sn(CH(SiMe_3)_2]_2$. Since the number of metal centered electron pairs and vacant orbitals in the SnR_2 and GaR_2^- monomeric units is identical, analogous modes of bonding can be proposed. The gallium dimer would have the equivalent of a bent gallium-gallium double bond, which results from a pairwise orbital overlap scheme bet-ween the filled non-bonding orbital of one $Ga(CH_2SiMe_3)_2^-$ unit with the vacant orbital of the other. This bonding scheme requires the gallium
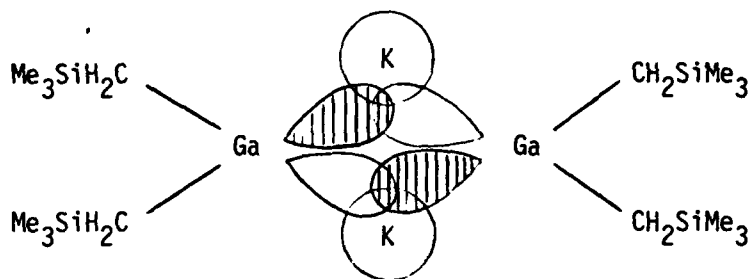
Figure 1

Proposed Structure and Bonding Scheme for $[KGa(CH_2SiMe_3)_2]_2$

(I) atoms to function simultaneously as both a Lewis acid and base, a condition which leads to "synergic bonding". The potassium atoms are most likely situated near the sites of orbital overlap between the two gallium atoms. Bonding might involve a 3-centered interaction. The nature of the (trimethylsilyl)methyl groups could provide a hydrocarbon sheath around the periphery of the molecule and possibly cover the potassium atoms. Thus, intermolecular interactions between the dimeric units would be minimized. The existence of metal-metal bonding in gallium chemistry is well documented. Gallium metal consists of dimeric (Ga_2) units arranged in deformed sets of hexagonal rings.[17] The anion,[18] $[Cl_3Ga-GaCl_3]^{2-}$, has been prepared by the anodic oxidation of gallium metal in 6 M HCl. The dioxane adduct of Ga_2Cl_4, $[GaCl_2 \cdot O_2C_4H_8]_2$, has a structure which incorporates a gallium-gallium bond.[19] In the last

two examples, the metal-metal bond was verified by a Raman band around 235 cm^{-1}. Similar attempts to confirm the gallium-gallium bond in the new ((trimethylsilyl)methyl)gallium (I) derivatives were thwarted by the extremely low quality of Raman spectra due to high florescence.

The second possible mode of molecular association is by three-centered electron-deficient alkyl bridge bonding as shown by the following structure. However, this type of bonding is inconsistent with our
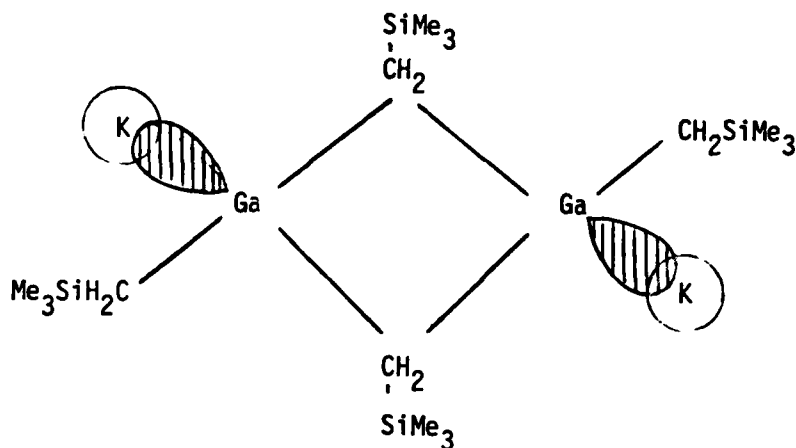
experimental data, including the lack of reaction between $[KGa(CH_2SiMe_3)_2]_2$ with amines and strong oxygen bases, and ^1H NMR chemical shift data for solutions containing these types of bases. The details of these experimental results are discussed in a following section. Bridge bonding has not been previously observed in gallium chemistry.[2] There are no alkyl substituted gallium compounds which are associated in solution by alkyl bridge bonding. Lastly, it is important to realize that the proposed electron precise gallium-gallium bonds in the low oxidation state compounds should be energetically more favorable than electron-deficient alkyl bridge bonds.

The proposed structure for the trimer, $[NaGa(CH_2SiMe_3)_2]_3$, (Figure 2) is closely related to the proposed structure of $[KGa(CH_2SiMe_3)_2]_2$. The addition of another monomeric $Ga(CH_2SiMe_3)_2$ unit to the dimer leads to a triangular arrangement of gallium atoms linked by gallium-gallium single bonds. The sodium atoms would be similarly placed near sites of orbital overlap between gallium atoms and occupy positions along the edges of the gallium atom triangle. The smaller size and stronger bonding interactions of the sodium atoms compared with potassium might be responsible for the observed increase in degree of molecular association. Since the structure and nature of bonding of the dimer and trimer are very closely related, similar chemical and physical properties are observed. It is noteworthy that the structures proposed for
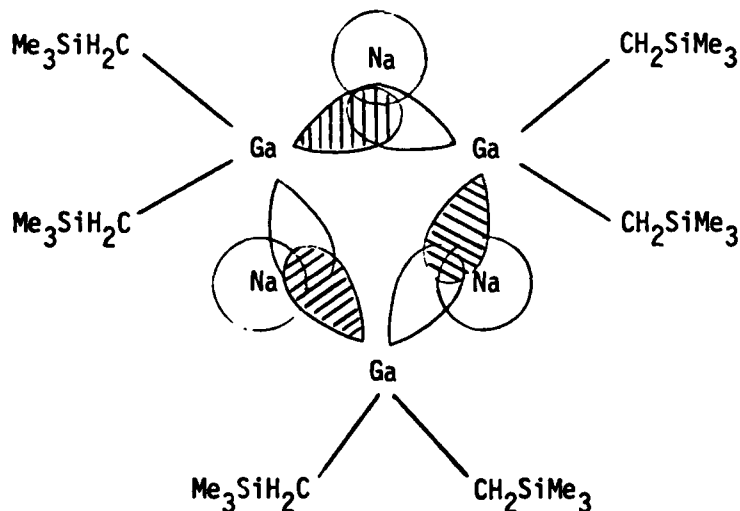

Figure 2

Proposed Structure and Bonding Scheme for $[NaGa(CH_2SiMe_3)_2]_3$.

the dimer and trimer are analagous to the type observed for the rhenium halides,[20,21,22] $Re_2Cl_8^{2-}$ and Re_3Cl_9.

The NMR spectral data are fully consistent with the proposed structures. Since the (trimethylsilyl)methyl groups in $[KGa(CH_2SiMe_3)_2]_2$ and $[NaGa(CH_2SiMe_3)_2]_3$ occupy magnetically equivalent positions, only two sharp lines are observed in both the ^1H and ^{13}C NMR spectra for each compound (Table III). One line is assigned to the methyl-hydrogen or -carbon atoms whereas the second line corresponds to the methylene-hydrogen or -carbon atoms. It is interesting that the methylene proton resonance shifts to higher field as the molecular association increases from dimer to trimer. These data would suggest that the methylene protons have more negative charge due to the inductive effects in a nominally trianionic species compared to a dianionic species. However, further comparisons with $Ga(CH_2SiMe_3)_3$ in order to determine the effects of oxidation state on NMR chemical shift would not be valid because the coordination number around gallium has changed significantly. In the potassium dimer gallium has an apparent coordination number of five whereas in the sodium trimer it is six, and in $Ga(CH_2SiMe_3)_3$ it is only three. Similarly, direct comparisons of infrared frequencies assigned to the gallium-carbon stretching modes for the various ((trimethylsilyl)-methyl)gallium compounds are also unwarranted.

The behavior of $[NaGa(CH_2SiMe_3)_2]_3$ and $[KGa(CH_2SiMe_3)_2]_2$ as Lewis acids towards the Lewis bases, diethylether, dimethoxyethane, tetrahydrofuran, acetonitrile and trimethylamine, was investigated in order to determine the relative strength and primary site of reaction, the alkali-metal ion or the gallium (I) atom. Our data suggest that

$[NaGa(CH_2SiMe_3)_2]_3$ is the stronger acid and the base reacts primarily with the alkali metal ion. These conclusions are based on the range of bases which form stable 1.1 adducts at room temperature with a given acid and the relative ^1H NMR chemical shift data. The potassium derivative formed a stable adduct with only dimethoxyethane whereas the sodium compound formed adducts with dimethoxyethane, tetrahydrofuran and trimethylamine. Similarly, the dimethoxyethane protons exhibit larger changes in NMR chemical shifts upon coordination to the sodium compound than the potassium compound. However, it is interesting to note that for the bases studied the protons in tetrahydrofuran exhibit the largest change in chemical shift upon coordination but the magnitude is still small (0.25 ppm downfield) in comparison with the effects of the stronger Lewis acid,[13] $[Ga(CH_2SiMe_3)_2Br]_2$ (0.47 ppm). It is also noteworthy that the chemical shift of the methyl (N) protons for free $N(CH_3)_3$ and $NaGa(CH_2SiMe_3)_2 \cdot N(CH_3)_3$ are identical. All of these data suggest that the base coordinates with the alkali metal ion. If the base had coordinated to the gallium (I), the change in alkali-metal ion should have had a minor affect on the Lewis acidity of the low oxidation state compound. Furthermore, ethers are stronger bases than amines towards the alkali-metal ions whereas amines are usually stronger bases to gallium.[2] The anionic character of the $Ga(CH_2SiMe_3)_2^-$ moiety is probably responsible for the weak Lewis acidic behavior. An X-ray structural study[23] of $[NaBe(C_2H_5)_2 \cdot O(C_2H_5)_2]_2$ has shown the ether to be bound exclusively to the sodium ions rather than the beryllium atoms. Reactions of the gallium (I) anions as Lewis bases will be the subject of future publications.

The dimethoxyethane adduct, $NaGa(CH_2SiMe_3)_2 \cdot MeOC_2H_4OMe$, was further

characterized by cryoscopic molecular weight measurements in benzene solution. The apparent molecular weight depends upon the concentration of the solution. At higher concentrations, a molecular weight corresponding to the timer was observed. At the lowest concentration, the degree of association was 1.69. These data would suggest that either an equilibrium between monomer, dimer and trimer exists in solution, or alternatively, the $[NaGa(CH_2SiMe_3)_3]_3$ trimer remains in tact but with various numbers of bound dimethoxyethane molecules. The lithium derivative, $LiGa(CH_2SiMe_3)_2 \cdot MeOC_2H_4OMe$, was also prepared but it was not sufficiently soluble in benzene for molecular weight measurements. Therefore, a structural hypothesis is not warranted at this time.

The successful synthesis of a low oxidation state organometallic anion of gallium opens a new area of chemistry. Periodic trends can be used to predict that analagous compounds might exist for indium and possibly aluminum. Similarly, the available electron pair on the main-group metal atom in the low oxidation state also implies the potential for nucleophilic reaction chemistry. Such aspects of the chemistry of these metal-based anions are being actively pursued.

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